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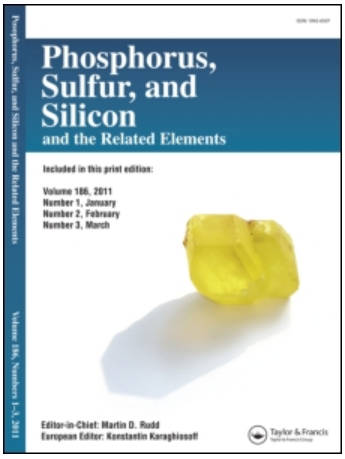

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Triphenylphosphine Mediated Simple Synthesis of Vinyl-Substituted Benzimidazoles

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TRIPHENYLPHOSPHINE MEDIATED SIMPLE SYNTHESIS OF VINYL-SUBSTITUTED BENZIMIDAZOLES

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N-*isopropenylbenzimidazolone undergoes a smooth reaction with triphenylphosphine and dialkyl acetylenedicarboxylates to produce highly functionalized salt-free phosphorus ylides in good yields. These stabilized phosphorus ylides exist as a mixture of two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. These ylides are converted to dialkyl 2-(1-isopropenyl-1H-benzimidazol-2-yl)-but-2-enedioates in boiling toluene.*

Keywords: Intramolecular Wittig reaction; NH-acid; *N*-isopropenylbenzimidazolone; triphenylphosphine

INTRODUCTION

The development of simple synthetic routes for widely used organic compounds from readily available starting materials is one of the major tasks in organic synthesis.[1] Benzimidazolones are of interest because they constitute an important class of natural and nonnatural products, many of which exhibit biological activity.[2–5] The interest in 2-substituted benzimidazolones stems from the appearance of such systems in useful drugs. Consequently, there has been an ongoing interest in the synthesis of 2-substituted benzimidazolones.[2–7]

As part of our current studies on the development of new routs to hetrocyclic and carbocyclic systems,[8–10] we now report on the reaction

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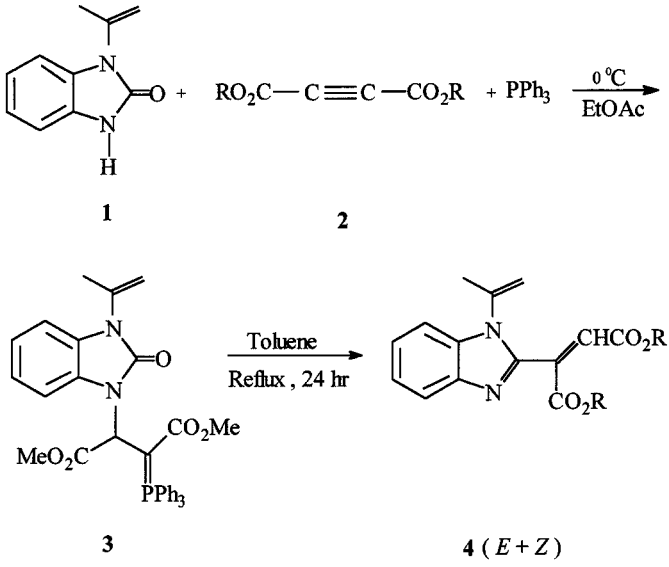
between *N*-isopropenylbenzimidazolone (**1**) and dialkyl acetylenedicarboxylate (**2**) in the presence of triphenylphosphine. Thus, reaction of NH-acid **1** with acetylenic esters **2** leads to stable phosphorus ylides **3**. These stable vinylphosphoranes undergo an intramolecular Wittig reaction,[11–13] followed by ring opening, in boiling toluene to yield dialkyl 2-(1-isopropenyl-1*H*-benzimidazol-2-yl)-but-2-enedioates **4** in good yields (Scheme 1).



1 **2** **3** **4** (*E* + *Z*)

2-4	R	% Yield of 3	% Yield of 4	*E* : *Z*
a	Me	96	62	80:20
b	Et	98	54	90:10
c	*t*-Bu	95	65	>98%*E*

SCHEME 1

RESULTS AND DISCUSSION

The reaction of *N*-isopropenylbenzimidazolone with dialkyl acetylenedicarboxylate (**2**) in the presence of triphenylphosphine proceeded spontaneously at room temperature in ethyl acetate and was finished within a few hours. ^{1}H and ^{13}C NMR spectra of the crude product cleanly indicated the formation of dialkyl 2-(3-isopropenyl-2-oxo-2,3-dihydrobenzimidazol-1-ly)-3-[(triphenyl-λ^5-phosphanylidene)]-butanedioate (**3**).

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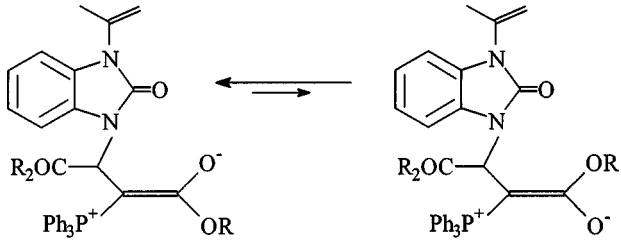
Any product other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–c** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these ylides are fairly similar and display molecular ion peaks. Any other fragmentation involved the loss of the ester moieties.

The NMR spectra of ylides **3a–c** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation aboat the partial double bond in (*E*)-**3** and (*Z*)-**3** geometrical isomers is slow on the NMR timescale at ambient temperature. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–c** are shown in Table I. Assignment of configuration (*Z*) to the major geometrical isomer is based on the ^{1}H chemical shift of the OR moiety, which is expected to be shielded as a result of the anisotropic effect of the phenyl groups (see Scheme 2).



(*Z*)-**3**; Major (*E*)-**3**; minor

SCHEME 2

The methoxy region of the ^{1}H NMR spectrum of **3a** in $CDCl_3$ at ambient temperature (25°C) exhibits two sharp singlets for the CO_2CH_3 groups of (*E*) and (*Z*) isomers and two fairly broad singlets for the OCH_3 groups (see Table I). Near 5°C the broad lines become sharper. The ^{1}H NMR spectrum of **3a** in 1,2-dichlorobenzene at 25°C is similar to that measured in $CDCl_3$ (see Table II). Increasing the temperature results in coalescence of the OCH_3 resonances. At 110°C, a fairly broad singlet was observed for the OCH_3 group, while the CO_2CH_3 protons apear as a sharp single resonance.

Although, an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **3a** was not undertaken, the variable temperature spectra allowed to calculate[14] the free energy barrier (if not the enthalpy and entropy of activation) for the dynamic NMR process in this ylide (see Table II). The experimental data available are

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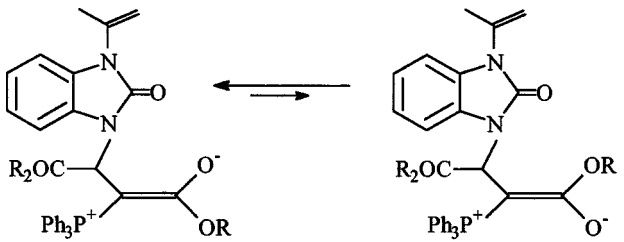


TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2 and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds **3a–c**

		^{1}H NMR spectroscopic data			^{13}C NMR data		
Compound	Isomer (%)	H-2 ($^{3}J_{PH}$)	OR	CO_2R	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	^{31}P NMR
3a	M (67)	5.36 (16.0)	3.23	3.68	56.10 (16.0)	40.68 (123.0)	24.55
	m (33)	5.25 (16.0)	3.63	3.71	56.47 (16.0)	41.12 (132.0)	25.32
3b	M (75)	5.31 (17.0)	3.68–3.86[a]	4.05–4.35[a]	56.30 (18.0)	41.10 (126.0)	24.52
	m (25)	5.18 (17.0)	4.05[a]	4.35[a]	56.15 (18.0)	41.20 (126.0)	25.58
3c	M (>95%)	5.15 (16.0)	1.01	1.5	56.45 (17.0)	39.72 (124.0)	24.17

[a]The methylene protons of the or moiety.

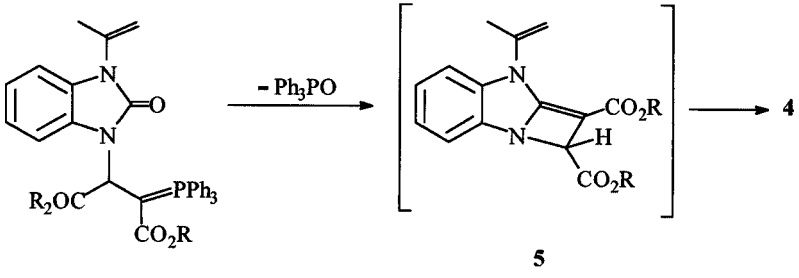
TABLE II Selected Proton Chemical Shifts (at 300 MHz, in ppm, Me_4Si) and Activation Parameters (kJ mol^{-1}) for **3a** in 1,2-Dichlorobenzene

Temp (°C)	Resonance (P—C—CO_2CH_3)		$\Delta\nu$ (Hz)	k (s^{-1})	T_c (K)	$\Delta G^{\#}$
25	3.23	3.63	120	266	353	70.53 ± 2
110	3.32					

not suitable for obtaining meaningful values of $\Delta H^{\#}$ and $\Delta S^{\#}$, even though the errors in $\Delta G^{\#}$ are not large.[15]

Phosphorus ylides **3** undergo a smooth reaction in boiling toluene to produce triphenylphosphine oxide and dialkyl 2-(1-isopropenyl-1*H*-benzimidazol-2-yl)-but-2-enedioates **4** (see Scheme 1). Structure **4** was assigend to the isolated products on the basis of their elemental analyses and IR, ^1H, and ^{13}C NMR and mass spectral data. Thus, the ^1H NMR spectrum of each of the isolated products exhibited a vinylic methine proton singal at $\delta = 6.48$–7.24. Further evidence was obtained from the ^{13}C NMR spectra, which displayed characteristic resonances in agreement with structure **4**. The mass spectra of **4a–c** are similar as expected, and confirm their molecular weights. Partial asignments of the ^1H and ^{13}C resonances in the ^1H, and ^{13}C NMR spectra of **4a–c** are given in the experimental section.

Although we have not yet established the mechanism of the thermal conversion of **3** to **4** in an experimental manner, a possible explanation is indicated in Scheme 3 on the basis of the well-established chemistry of the Wittig reaction.[11,12] It is reasonable to assume that compound **4** results from an initial intramolecular Wittig reaction of phosphorane **3** and a subsequent electrocyclic ring opening reaction of the cyclobutene derivative **5** (see Scheme 3).



5

SCHEME 3

In summary, the presented method carries the advantage of being performed under neutral conditions and requiring no activation or modification of the educts. We anticipate that the reactions described herein

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represent a simple entry into the synthesis of polyfunctional benzimidazole derivatives of potential interest.

EXPERIMENTAL

N-isopropenylbenzimidazolone was prepared by dry fusion of equimolar amounts of *o*-phenylenediamine and ethyl acetoacetate.[16] Dialkyl acetylenedicarboxylates (**2**), *o*-phenylenediamine, ethyl acetoacetate, and triphenylphosphine were obtained from Merck-Schuchardt and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with Bruker Spectrospin at 300, 75, and 121.4 MHz respectively. Mass spectra were recorded on a Hewlet-Packard MSD 5973 mass spectrometer. IR spectra were measured on a Bomem MB-100 IR spectrometer.

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Preparation of Di-methyl 2-(3-isopropenyl-2-oxo-2,3-dihydro-benzimidazol-1-yl)-3-[(triphenyl-λ^5-phosphanylidene)]-butanedioate 3a

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.52 g, 2 mmol) and *N*-isopropenylbenzimidazolone (0.35 g, 2 mmol) in ethyl acetate (15 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (2 mmol) in ethyl acetate (4 mL) at −5°C over 15 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 2 h. The solid product was filterd and washed with cold ethyl acetate (5 mL).

Selected data for dimethyl 2-(3-isopropenyl-2-oxo-2,3-dihydro-benzimidazol-1-yl)-3-[(triphenyl-λ^5-phosphanylidene)]-butanedioate ***3a***. White solid (0.87 g), yield 92%, m.p. 212–214°C (Found: C, 70.57; H, 5.42; N, 4.84, $C_{34}H_{31}N_2O_5P$ requires C, 70.58, H, 5.40, N, 4.84%): IR (KBr) (ν_{max}/cm^{-1}): 1645, 1705 and 1759 (C=O); MS (*m/z*, %): 405 (20), 368 (10), 353 (9), 339 (11), 277 (10), 262 (100), 183 (75), 152 (12), 108 (23), 83 (11), 57 (15), 43 (12). ^{1}H, ^{13}C, and ^{31}P NMR data for the major (67%) isomer (*Z*)-**3a**: δ_H 2.04 (3 H, s, CH_3), 3.23 and 3.68 (6 H, s, 2 OMe), 5.15 and 5.22 (2 H, s, CH_2=C), 5.36 (1 H, d, $^{3}J_{PH} = 16$ Hz, *N*–CH), 7.00 and 7.20 (3 H, m, 3 CH of C_6H_4), 7.36–7.70 (15 H, m, 3 C_6H_5), 7.78 (1 H, d, $^{3}J = 8$ Hz, CH of C_6H_4); δ_C 20.60 (CH_3), 40.68 (d, $^{1}J_{PC} = 123$ Hz, P=C), 49.70 and 53.00 (2 OMe), 56.10 (d, $^{2}J_{PC} = 16$ Hz, P–C–CH), 108.54 (s, CH_2=C), 112.08, 120.92, 121.97 and 126.14 (4 CH of C_6H_4),

126.80 (d, $^1J_{PC} = 91$ Hz, P-C_{ipso}), 129.25 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.55 (d, $^4J_{PC} = 3$ Hz, C_{para}), 133.90 (d, $J_{PC} = 7$ Hz, C_{ortho}), 138.55 (C=CH_2), 152.10 (C=O), 171.00 (d, $J_{PC} = 13$ Hz, C=O), 172.10 (d, $J_{PC} = 15$ Hz, C=O); δ_p 24.55 (C=PPh_3).

^{1}H, ^{13}C, and ^{31}P NMR data for the minor (33%) isomer (*E*)-**3a**: δ_H 2.08 (3 H, s, CH_3), 3.70 and 3.80 (6 H, s, 2 OMe), 5.10 and 5.25 (2 H, s, CH_2=C), 5.25 (1 H, d, $^3J_{PH} = 16$ Hz, *N*–CH), 7.00 and 7.20 (3 H, m, 3 CH of C_6H_4), 7.36–7.70 (15 H, m, 3 C_6H_5), 7.78 (1 H, d, $^3J = 8$ Hz, CH of C_6H_4); δ_C 20.65 (CH_3), 41.12 (d, $^1J_{PC} = 132$ Hz, P=C), 50.70 and 52.80 (2 OMe), 56.47 (d, $^2J_{PC} = 16$ Hz, P–C–CH), 108.76 (CH_2=C), 112.00, 113.10, 121.59 and (4 CH of C_6H_4), 126.06 (d, $^1J_{PC} = 91$ Hz, P-C_{ipso}), 129.26 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.60 (d, $^4J_{PC} = 2.3$ Hz, C_{para}), 134.01 (d, $^2J_{PC} = 9$ Hz, C_{ortho}), 138.65 (C=CH_2), 152.35 (C=O), 171.80 (d, $^3J_{PC} = 13$ Hz, C=O), 172.20 (d, $^3J_{PC} = 15$ Hz, C=O); δ_p 25.32 (C=PPh_3).

Selected data for diethyl 2-(3-isopropenyl-2-oxo-2,3-dihydrobenzimidazol-1-yl)-3-[(triphenyl-λ^5-phosphanylidene)]-butanedioate ***3b***. White solid (1.0 g), yield 98%, m.p. 175–177°C (Found: C, 70.93; H, 5.3; N, 4.62, $C_{36}H_{35}N_2O_5P$ requires C, 71.27; H, 5.28; N, 4.62%): IR (KBr) (ν_{max}/cm^{-1}): 1636, 1707 and 1743 (C=O); MS (*m*/*z*, %): 262 (100), 183 (74), 152 (12), 108 (23), 57 (15), 43 (13). ^{1}H, ^{13}C, and ^{31}P NMR data for the major (75%) isomer (*Z*)-**3b**: δ_H 0.50 (3 H, t, CH_3), 1.30 (3 H, t, CH_3), 2.05 (3 H, s, CH_3), 3.68–3.86 (2 H, AB quartet, CH_2), 4.05–4.35 (2 H, AB quartet, CH_2), 5.06 and 5.23 (2 H, 2 br s, C=CH_2), 5.31 (1 H, d, $^3J_{PH} = 17$ Hz, N–CH), 7.03–7.17 (3 H, m, 3 CH of C_6H_4), 7.37–7.70 (15 H, m, 3 C_6H_5), 7.82 (1 H, d, J = 2 Hz, CH of C_6H_4); δ_C 14.44 and 14.65 (2 CH_3), 20.68 (CH_3), 41.10 (d, $^1J_{PC} = 126$ Hz, P=C), 56.30 (d, $^2J_{PC} = 18$ Hz, P–C–CH), 58.30 and 61.60 (2 OCH_2), 108.40 (CH_2=C), 112.70, 113.00, 120.80 and 121.40 (4 CH of C_6H_4), 127.00 (d, $^1J_{PC} =$ 90 Hz, P-C_{ipso}), 129.10 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.45 (d, $^4J_{PC} = 3$ Hz, C_{para}), 134.00 (d, $^2J_{PC} = 10$ Hz, C_{ortho}), 138.75 (C=CH_2), 152.30 (C=O, imide), 169.55 (d, $J_{PC} = 12$ Hz, C=O), 171.45 (d, $J_{PC} = 15$ Hz, C=O); δ_p 24.52 (C=PPh_3).

^{1}H, ^{13}C, and ^{31}P NMR data for the minor (25%) isomer (*E*)-**3b**: δ_H 1.24 (3 H, t, CH_3), 1.34 (3 H, t, CH_3), 2.07 (3 H, s, CH_3), 4.05–4.35 (4 H, AB quartet, CH_2), 5.10 and 5.26 (2 H, 2 br s, C=CH_2), 5.18 (1 H, d, $^3J_{PH} = 17$ Hz, N–CH), 7.03–7.17 (3 H, m, 3 CH of C_6H_4), 7.37–7.70 (15 H, m, 3 C_6H_5), 7.82 (1 H, d, $J = 2$ Hz, CH of C_6H_4); δ_C 14.58 and 15.24 (2CH_3), 20.61 (CH_3), 41.20 (d, $^1J_{PC} = 126$ Hz, P=C), 56.15 (d, $^2J_{PC} = 18$ Hz, P–C–CH), 59.10 and 61.60 (2 OCH_2), 108.70 (CH_2=C), 112.70, 113.00, 120.80 and 121.40 (4 CH of C_6H_4), 126.35 (d, $^1J_{PC} =$ 90 Hz, P-C_{ipso}), 129.20 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.50 (d, $^4J_{PC} = 3$ Hz, C_{para}), 134.00 (d, $^2J_{PC} = 10$ Hz, C_{ortho}), 138.65 (C=CH_2), 152.45

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(C=O, imide), 170.70 (d, $J_{PC} = 12$ Hz, C=O), 171.45 (d, $J_{PC} = 15$ Hz, C=O); δ_p 25.58 (C=PPh_3).

Selected data for di-tert-Buthyl 2-(3-isopropenyl-2-oxo-2, 3-dihydro-benzimidazol-1-yl)-3-[(triphenyl-λ^5-phosphanylidene)]-butanedioate ***3c***. White solid (1.0 g), yield 80%, m.p. 206–209°C (Found: C, 72.42; H, 6.54; N, 4.32, $C_{40}H_{43}N_2O_5P$ requires C, 72.49, H, 6.54, N, 4.23%): IR (KBr) (ν_{max}/cm^{-1}): 1638, 1707 and 1744 (C=O). MS (*m/z*, %): 371 (99), 262 (100), 204 (9), 287 (11), 183 (77), 152 (12), 134 (18), 108 (25), 57 (25), 41 (14). ^1H, ^{13}C, and ^{31}P NMR data for the major (>95%) isomer (*Z*)-**3c**: δ_H 1.01 (9 H, s, CMe_3), 1.50 (9 H, s, CMe_3), 1.61 (3 H, s, CH_3), 5.06 and 5.18 (2 H, 2 br s, CH_2=C), 5.15 (1 H, d, $^3J_{PH} = 16$ Hz, N–CH), 7.00 and 7.20 (3 H, m, 3 CH of C_6H_4), 7.35–7.70 (15 H, m, 3 C_6H_5), 7.97 (1 H, d, $J = 8$ Hz, CH of C_6H_4); δ_C 20.74 (CH_3), 28.63 and 28.81 (2 CMe_3), 39.72 (d, $^1J_{PC} = 124$ Hz, P=C), 56.45 (d, $^2J_{PC} = 17$ Hz, P–C–CH), 77.75 and 81.02 (2 CMe_3), 108.42 (CH_2=C), 111.85, 112.73, 120.53 and 121.97 (4 CH of C_6H_4), 127.45 (d, $^1J_{PC} = 91$ Hz, P-C_{ispo}), 128.95 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 129.07 and 129.31 (2 C), 132.30 (d, $^4J_{PC} = 2$ Hz, C_{para}), 134.06 (d, $^2J_{PC} = 10$ Hz, C_{ortho}), 138.91 (C=CH_2), 152.05 (C=O, imide), 168.08 (d, $J_{PC} = 12$ Hz, C=O), 170.09 (d, $J_{PC} = 14.5$ Hz, C=O); δ_p 24.17 (C=PPh_3).

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Preparation of Dimethyl 2-(1-isopropenyl-1H-benzimidazol-2-yl)-but-2-enedioate 4a

General Procedure

A magnetically stirred solution of phosphorous ylide **3a** (2.0 g, 3 mmol) in toluene (20 mL) was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was purified by (silica gel Merck 60 F_{254} mesh) thin layer chromatography in two steps using diethyl ether and hexane as eluents. Compound **4a**, yellow oil, was obtained as mixture of *Z*/*E* isomers.

Selected data for dimethyl 2-(1-isopropenyl-1H-benzimidazol-2-yl)-but-2-enedioate ***4a***. (Found: C, 63.7; H, 5.2; N, 9.4, $C_{16}H_{16}N_2O_4$ requires C, 63.99; H, 5.37; N, 9.33%): IR (KBr) (ν_{max}/cm^{-1}): 1713 (C=O). MS (*m/z*, %): 284 (25), 257 (56), 216 (30), 198 (27), 157 (21), 90 (37), 59 (19), 41 (28). ^1H and ^{13}C NMR data for the major (80%) isomer (*E*)-**4a**: δ_H 2.24 (3 H, s, CH_3), 3.69 and 3.87 (6 H, s, 2 OMe), 5.28, 5.39 (2 H, S, CH_2=C), 7.21 (1 H, s, CH=C), 7.04–7.28 (4 H, m, 4 CH of C_6H_4); δ_C 20.43 (CH_3), 52.77 and 53.81 (2 OMe), 109.54 (CH_2=C), 09.54, 109.81, 122.28 and 122.76 (4 CH of C_6H_4), 128.59 (CH=C), 129.30 and 129.78 (2 CH of C_6H_4), 138.10 (CH_2=C), 138.10, 133.51 (C=CH, C=N), 163.32 and 163.58 (2 C=O, ester).

^{1}H and ^{13}C NMR data for the major (20%) isomer (Z)-**4a**: δ_H 2.21 (3 H, s, CH_3), 3.83 and 3.95 (6 H, s, 2 OMe), 5.26 and 5.43 (2 H, S, CH_2=C), 6.48 (1 H, s, CH=C), 7.04–7.28 (4 H, m, 4 CH of C_6H_4); δ_C 20.29 (CH_3), 52.82 and 53.84 (2 OMe), 109.45 (CH_2=C), 109.45, 110.42, 122.08 and 122.95 (4 CH of C_6H_4), 128.78 (CH=C), 130.05 and 130.35 (2 CH of C_6H_4), 138.20 (C=CH_2), 138.20, 133.44 (C=CH, C=N), 163.61 and 165.43 (2 C=O, ester).

Selected data for diethyl 2-(1-isopropenyl-1H-benzimidazol-2-yl)-but-2-enedioate ***4b***. (Found: C, 65.6; H, 6.1; N, 8.9, $C_{18}H_{20}N_2O_4$ requires C, 65.84; H, 6.14; N, 8.53%): IR (KBr) (ν_{max}/cm^{-1}): (C=O). ^{1}H and ^{13}C NMR data for the major (90%) isomer (*E*)-**4b**: δ_H 1.12 (3 H, t, CH_3), 1.32 (3 H, t, CH_3), 2.26 (3 H, s, CH_3), 4.13 and 4.35 (4 H, q, 2 OCH_2), 5.28 and 5.39 (2 H, s, CH_2=C), 7.24 (1 H, s, C=CH), 6.80, 7.05–7.75 (3 H, m, 3 CH of C_6H_4); δ_C 14.25 and 14.48 (2 CH_3), 20.49 (CH_3), 61.85 and 63.16 (2 OCH_2), 109.64 (CH_2=C), 109.80, 114.00, 122.27 and 122.74 (4 CH of C_6H_4), 134.03 (CH=C), 132.57 and 132.21 (2 CH of C_6H_4), 137.55 (CH_2=C), 129.79 and 137.55 (C=CH, C=N), 162.80 and 163.20 (2 C=O, ester).

^{1}H and ^{13}C NMR data for the minor (10%) isomer (*E*)-**4b**: δ_H 1.39 (3 H, t, CH_3), 1.30 (3 H, t, CH_3), 2.22 (3 H, s, CH_3), 4.30 and 4.45 (4 H, q, 2 OCH_2), 5.28 and 5.41 (2 H, s, CH_2=C), 6.51 (1 H, s, C=CH), 6.80 and 7.05–7.75 (3 H, m, 3 CH of C_6H_4); δ_C 14.25 and 14.58 (2 CH_3), 20.35 (CH_3), 61.71 and 62.96 (2 OCH_2), 110.15 (CH_2=C), 110.60, 115.00, 116.20 and 124.00 (4 CH of C_6H_4), 133.62 (CH=C), 132.21 and 132.44 (2 CH of C_6H_4), 137.69 (C=CH_2), 130.32 and 133.62 (C=CH, C=N), 163.10 and 165.00 (2 C=O, ester).

Selected data for di-tert-buthyl 2-(1-isopropenyl-1H-benzimidazol-2-yl)-but-2-enedioate ***4c***. (Found: C, 68.5; H, 7.0; N, 7.1, $C_{22}H_{28}N_2O_4$ requires C, 68.73; H, 7.34; N, 7.29%): IR (KBr) (ν_{max}/cm^{-1}): 1656 and 1717 (C=O), 2932, 3056 and 3002 (=C–H). ^{1}H and ^{13}C NMR data for the major (>98%) isomer (*E*)-**4c**: δ_H 1.28 and 1.510 (18 H, s, 2 CMe_3), 2.15 (3 H, s, CH_3), 5.24 and 5.36 (2 H, s, CH_2=C), 7.05 (1 H, s, C=CH), 6.80 and 7.00–7.20 (4 CH of C_6H_4); δ_C 20.53 (CH_3), 28.07 and 28.22 (2 CMe_3), 82.70 and 83.90 (2 $OCMe_3$), 109.56 (CH_2=C), 109.60, 113.75, 122.10 and 122.50 (4 CH of C_6H_4), 128.85 and 128.95 (2 CH of C_6H_4), 129.99 (CH=C), 138.25 (C=CH_2), 137.51 and 137.66 (C=CH, C=N), 161.72 and 162.86 (2 C=O, ester).

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